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Normal coordinate treatment of some pyridines

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Abstract . A 53-parameter modified valence force field has been obtained for pyridine, pyridine-d5 and 2,6-difluoro pyridine. The force constants have been refined using vibrational frequencies employing Overlay-least-squares technique. Eigen vectors and potential energy distributions were computed They have been used to propose unambiguous vibrational assignments for both in-plane and out-of-plane vibrational frequencies of the three molecules. On this basis certain assignments proposed by earlier workers have been revised.

Keywords · Normal coordinate treatmart, force constants, potential energy distribution.

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1. Introduction

Long *et al* [1] made zero-order nonnal coordinate calculations for pyridine (PYR) and pyridine-d5 (PYR-d5) by transfering valence force constants from benzene. These computations suffer from the following short-comings.

(i) Nitrogen atom in the benzene ring was treated as ^{14}C as far as the force constants are concerned.

(ii) The angle between the *i*-th C–H bond and the exterior bisector of the C–C–C angle (or C–C–N angle) centred on the *i*-th carbon atom was defined as the internal coordinate B_i, which account for C–H in-plane bending vibrations. This has been discarded in the contemporary literature by defining B's interms of CCH angles themselves. Hence there is a need to incorporate this aspect into the computations.

(iii) The forece constants were not refined. Hence they can at best be an approximation.

Therefore, we thought it worthwhile to re-do normal coordinate analysis for PYR and PYR-d5 eliminating the above drawbacks. In order to increase the number of data used in the calculations we have included 2,6-difluoro pyridine (DFP) for which an approximate normal coordinate analysis is available in literature [2].

2. Normal coordinate treatment and results

The molecules under investigation possess c_{2v} point group symmetry. In the c_{2v} structure the 27 fundamentals of each of the three molecules are distributed as $10A_1 + 9B_2 + 3A_2 + 5B_1$. The modes belonging to A_1, B_1 and B_2 species are active both in infrared and Raman spectra, whereas the A_2 modes are active in Raman and forbidden in infrared. The structure parameters used are γ(C–C) = 1.397 A, γ(C–N) = 1.397 A, γ(C–H) = 1.09 A, γ(C–F) = 1.327 A and $\angle$CCC = $\angle$CCN = $\angle$CNC = $\angle$CCH = $\angle$CCF = 120°. Internal coordinates and symmetry coordinates used in the computations were adopted from monohalogenated nitrobenzenes [3] with suitable modifications for the present case. The initial force constants were trasferred from the final values reported in reference 3 and substituted anisoles [4]. The initial constants connected with CNC moiety were taken to be equal to that of CCC moiety. This initial set of 53 constants was subsequently refined through several cycles with a damping factor of 0.1 using overlay damped least-squares method [5]. The vibrational frequencies required for the purpose were taken from Green *et al* [6], and Bailey and Steele [2] for PYR and DFP, respectively and used those employed by Long [1] for PYR-d5. This allowed the approximate set of initial constants to adjust properly to the present set of molecules at the same

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time taking care of any correlations that may be present between certain constants. At this stage the damping factor was reduced to zero, all the interaction constants were fixed and refinement of 15 diagonal constants was continued using 78 vibrational frequencies of PYR, PYR-d5 and DFP. Under these conditions the refinement converged smoothly in three cycles with an average error of 11.1 cm^{-1} between the observed and calculated frequencies. The final set of force constants thus obtain is given in Table 1 alongwith initial values and dispersions. The observed and calculated frequencies, potential energy distributions and vibrational assignment of the three molecules are presented in Table 2.

Table 1. Force constants of pyridine, deuterated pyridine and difluoro pyridine (in mdyn/A, mdyn/rad and mdyn-A/rad^2)

No	Symbol	Coordinates involved	Common Atoms	Value		
				Initial*	Final	Dispersion
		(A) In-plane force constants				
		Diagonal force constants				
		Stretch				
1	K_d	CC	–	6.5957	6.3646	0.042
2	K_D	C–N	–	6.5957	6.6000	0.081
3	K_r	C–H	–	5.1860	5.0997	0.008
4	K_{r1}	C–F	–	6 2567	6.5060	0 127
		Bend				
5	H_θ	∠CCC	–	0.8866	1.0874	0.055
6	H_α	∠CNC	–	0.8866	1.0572	0 106
7	H_β	∠NCC	–	0.8866	1.2741	0.080
8	H_ϕ	∠CCH	–	0.5111	0 5546	0.006
9	$H_{\phi 1}$	∠NCH	–	0.5111	0.5269	0.019
10	$H_{\phi 2}$	∠CCF	–	0.8775	1.2593	0.114
11	$H_{\phi 3}$	∠NCF	–	0 8775	0.1382	0 080
		Interaction constants				
		Stretch-stretch				
12	$F^0_{(d,d)}$	C–C, C–C	C	0.9117	1.3080	0.0
13	$F^m_{(d,d)}$	C–C, C–C	–	–0.5506	–0.5521	0.0
14	$F^p_{(d,d)}$	C–C, C–C	–	0.1882	0 0843	0.0
15	$F_{(d,D)}$	C–C, C–N	C	0.9117	0 5805	0.0
16	$F_{(d,r)}$	C–C, C–H	C	–0.0264	–0.0124	0.0
17	$F_{(D,r)}$	C–N, C–H	C	–0.0264	0.2870	0.0
18	$F^0_{(r,r)}$	C–H, C–H	–	–0.0334	–0.0524	0.0
19	$F^m_{(r,r)}$	C–H, C–H	–	–0.0664	–0.0261	0.0
20	$F^p_{(r,r)}$	C–H, C–H	–	–0.0970	0.0273	0.0
21	$F_{(d,r1)}$	C–C, C–F	C	0.2383	0 8179	0 0
22	$F_{(D,r1)}$	C–N, C–F	C	0.2383	0.4165	0 0
23	$F_{(D,D)}$	C–N, C–N	N	0.9117	0.2438	0 0
		Stretch-bend				
24	$F_{(d,\theta)}$	C–C, ∠CCC	C–C	0.4178	0.3347	0 0
25	$F_{(d,\beta)}$	C–C, ∠NCC	C–C	0.4178	0.0240	0 0
26	$F_{(D,\alpha)}$	C–N, ∠CNC	C–N	0.4178	–0.1290	0 0
27	$F_{(D,\beta)}$	C–N, ∠NCC	C–N	0.4178	0.3230	0 0
28	$F_{(d,\phi)}$	C–C, ∠CCH	C–C	0.1573	0.1817	0 0
29	$F_{(D,\phi 1)}$	C–N, ∠NCH	C–N	0.1573	0.1854	0 0
30	$F_{(r,\phi)}$	C–H, ∠CCH	C–H	–0.0224	0.0449	0 0
31	$F_{(r,\phi 1)}$	C–H, ∠NCH	C–H	–0.0224	0.1297	0 0
32	$F_{(d,\phi 2)}$	C–C, ∠CCF	C–C	–0.0006	–0.4730	0 0
33	$F_{(D,\phi 3)}$	C–N, ∠NCF	C–N	–0.0006	0.3019	0 0
34	$F_{(r1,\phi 2)}$	C–F, ∠CCF	C–F	1.0059	1 1590	0 0
35	$F_{(r1,\phi 3)}$	C–F, ∠NCF	C–F	1 0059	0.5246	0 0
		Bend-bend				
36	$F_{(\theta,\theta)}$	∠CCC, ∠CCC	C–C	–0.0407	0 0860	0 0
37	$F_{(\alpha,\beta)}$	∠CNC, ∠NCC	C–N	–0.0407	–0.1789	0 0
38	$F_{(\theta,\beta)}$	∠CCC, ∠NCC	C–C	–0.0407	–0.0651	0 0
39	$F_{(\phi,\phi)}$	∠CCH, ∠CCH	C–C	0 0440	0.0449	0 0
40	$F_{(\phi,\phi 3)}$	∠CCH, ∠FCC	C–C	–0.0308	–0.3214	0 0
		(B) Out-of-plane force constants				
41	δ	C–C	–	0.3622	0.2781	0 0042
42	δ_1	C–N	–	0.3622	0.3059	0 0010
43	γ_R	C–H	–	0.4589	0.4628	0 0022
44	γ_{R1}	C–F	–	0.6576	0.6378	0 0103
45	$\gamma_{R,R}$	C–H, C–H	C–C	–0.0696	–0.0518	0.0
46	$\gamma_{R,R1}$	C–H, C–F	C–C	–0.0734	–0.0541	0 0
47	δ_j,δ_{j+1}	C–C, C–C	CCC	–0.0113	–0.0162	0.0
48	δ,γ_R	C–C, C–H	C–C	0.1805	0.1573	0 0
49	δ,δ_1	C–C, C–N	CCC	–0.0113	–0.0086	0.0
50	$\delta 1,\delta_1$	C–N, C–N	C–N	–0.0113	0.0196	0 0
51	δ_1,γ_R	C–N, C–H	C–C	0.1805	0.1473	0 0
52	δ,γ_{R1}	C–C, C–F	C–C	0.2218	0.3243	0.0
53	δ_1,γ_{R1}	C–N, C–F	C–C	0.2218	0.0536	0.0

*Force constants at Nos. 18, 19 and 20 are taken from ref [4].

Table 2. Observed and calculated frequencies (in cm^{-1}) and vibrational assignment.

No	Mode	Frequency (cm⁻¹) PYR Obs.	PYR Calc.	PYR-d5 Obs.	PYR-d5 Calc.	2,6-DFP Obs.	2,6-DFP Calc.	Vibrational assignment[a]
				A_1-species				
1	ν(CH/CD) 2	3036	3035	2254	2261	3048	3043	100(2)
2	ν(CH/CD) 13/7*a*	3054	3262	2270	2276	3090	3073	99(13)
3	ν(CH/CD/CF) 20*a*	3054	3080	2285	2286	1310	1303	98(20*a*)
4	ν(CN) 1	992	997	962	963	736	739	79(1)
5	ν(CC) 8*a*	1583	1595	1542	1544	1592	1572	71(8*a*) + 25(9*a*)
6	ν(CC) 19*a*	1482	1486	1340	1352	1546	1526	66(18*a*) + 34(19*a*)
7	β(∠CCC) 6*a*	605	605	582	591	548	532	72(6*a*) + 13(9*a*)
8	β(∠CCC) 12	1068	1060	1006	1020	1074	1067	61(12) + 15(18*a*)
9	β(CH/CD/CF) 9*a*	1218	1213	908	873	245	243	65(9*a*) + 16(8*a*)
10	β(CH/CD) 18*a*	1030	1037	823	802	-	1008	64(1) + 31(18*a*)
				B_2-species				
11	ν(CH/CD/CF) 7*b*	3080	3086	2293	2290	998	988	98(7*b*)
12	ν(CH/CD) 20*b*	3036	3039	2254	2255	3107	3080	100(20*b*)
13	ν(CN) 8*b*	1572	1568	1530	1515	1614	1637	70(8*b*) + 30(18*b*)
14	ν(CC) 14	1375	1370	1322	1327	1284	1324	59(3) + 35(14)
15	ν(CC) 19*b*	1439	1442	1301	1265	1455	1457	40(19*b*) + 59(3)
16	β(∠CCC) 6*b*	652	649	625	628	568	560	61(6*b*) + 19(8*b*)
17	β(CH/CD) 3	1288	1299	-	1010	1233	1232	78(3) + 20(14)
18	β(CH/CD) 15/9*b*	1085	1092	887	891	1145	1142	42(19*b*) + 35(15)
19	β(CH/CD/CF) 18*b*	1148	1168	833	835	346	352	59(14) + 27(18*b*)
				A_2-species				
20	π(CH/CD/CF) 10*a*	891	851	690	669	501	500	100(10*a*)
21	π(CH/CD) 17*a*	986	975	798	787	876	876	100(17*a*)
22	π(∠CCCC) 16*a*	375	376	327	330	219	228	98(16*a*)
				B_1-species				
23	π(CH/CD) 5	942	981	823	826	993	960	100(5)
24	π(CH/CD/CF) 10*b*	886	911	762	739	-	277	100(10*b*)
25	π(CH/CD) 11	749	770	530	555	796	799	100(11)
26	π(∠CCCC) 4	700	679	567	597	720	718	100(4)
27	π(∠CCCC) 16*b*	405	412	371	371	469	463	100(16*b*)

[a] Results in this column correspond to PYR. The results of other molecules can be obtained from the author. Number before the parenthesis is % PED and number in the parenthesis is the mode in Wilson's notation [7].

- not observed.

3. Vibrational assignments

The assignments presented in Table 1 are self-explanatory. Hence the discussion is confined to certain important modes only.

3.1. *C–C and C–N stretching vibrations :*

The molecules described here, modes 8*a* and 8*b* are expected around 1600 cm^{-1}. The higher frequency has a large amount of C–C stretching character ranging from 70 to 84% in the three molecules investigated. As expected, it mixes with the C–H/C–D bending mode 9*a* and 9*b* in PYR and DFP, respectively, whereas it is pure in PYR-d5. The lower frequency is a C–C stretching mode to the extent of 70 to 80%. In PYR and PYR-d5, this mode mixes with C–H/C–D in-plane bending mode 18*b*, while in DFP it is pure. According to the calculations made here, the frequency of mode 8*a* is

greater than that of 8*b* in PYR and PYR-d5, whereas reverse is true in DFP. Thus the bands at 1583,1542 and 1592 cm^{-1} are ascribed to mode 8*a*, whereas those near 1572,1530 and 1614 cm^{-1} are attributed to vibration 8*b* in PYR, PYR-d5 and DFP, respectively.

The modes 19*a* and 19*b* are expected in the range 1400–1500 cm^{-1}. On the basis of calculations the bands at 1482, 1340 and 1546 cm^{-1} are assigned to mode 19*a*, while those around 1439, 1301 and 1455 cm^{-1} are attributed to mode 19*b* in PYR, PYR-d5 and DFP, repectively. The modes 19*a* and 19*b* mix with C–H/C–D in-plane bending modes 18*a* and 3, respectively in the three molecules.

The mode 14, called the Kekule mode, has been assigned around 1375, 1322 and 1284 cm^{-1} in PYR, PYR-d5 and DFP, respectively. This mode mixes with C–H/C–D in-plane bending vibrataion 3, 15 and 9*b* in PYR, PYR-d5 and DFP, respectively. It also mixes with C–F stretching mode 7*b* in DFP.

The assignment given for the C–C stretches in pyridine on the basis of present calculations is in agreement with that given by Green *et al* [6]. The modes 1 and 8*b* should be considered as the C–N stretching vibrations on the basis of % PED.

3.2. *Ring vibrations :*

The ring vibrations 1, 6*a*, 6*b* and 12 are identified and assigned on the basis of their characteristic eigen vector distribution. Let us consider the modes 6*a* and 6*b* corresponding to the benzene band at 606 cm^{-1}. According to normal coordinate analysis, the absorptions near 605, 582 and 548 cm^{-1} are due to the mode 6*a*, whereas those around 652, 625 and 568 cm^{-1} are attributed to mode 6*b* in PYR, PYR-d5 and DFP, respectively. The mode 6*a* mixes with C–H/C–D in-plane bending mode 9*a* in PYR and PYR-d5, whereas in DFP it mixes with C–C stretching mode 19*a*.

The absorptions near 1068, 1006 and 1074 cm^{-1} are attributed to vibration 12, whereas the fundamentals near 992, 962 and 736 cm^{-1} are ascribed to mode 1 in PYR, PYR-d5 and DFP, respectively. The mode 12 mixes with C–H/C–D in-plane bending vibration in the three molecules, whereas mode 1 is pure in PYR and PYR-d5, while it mixes with mode 12 and C–F stretching vibration 20*a* in DFP. The assignment for modes 12 and 18*a* in pyridine given by Green *et al* [6] is reversed in the present calculations.

3.3. *C–H/C–D/C–F in-plane bending vibrations :*

The modes 3, 9*a*, 18*a*, 18*b* and 15 designate the C–H and C–D in-plane bending vibration, in PYR and PYR-d5, whereas in DFP the C–H in-plane bending modes are designated as 3, 18*a* and 9*b*. The highest C–H/C–D in-plane bending vibration is mode 3. The bands near 1288, 1010 (calc. value) and 1233 cm^{-1} are due to mode 3 in PYR, PYR-d5 and DFP, respectively. This mode mixes with Kekule mode in PYR, whereas in PYR-d5 it is pure, while in DFP it mixes with C–F stretching mode 7*b* and mode C–C stretching mode 19b.

On the basis of calculations, the pair of bands at 1030 and 1148 cm^{-1}, and 823 and 833 cm^{-1} are attributed to modes 18*a* and 18*b*. Similarly, the modes 9*a* and 15 are identified near 1218 and 1085 cm^{-1} and 908 and 887 cm^{-1}, respectively in PYR and PYR-d5. The bands near 1145 and 1008 cm^{-1} (calc value) are ascribed to C–H in-plane bending modes 9*b* and 18*a* in DFP. As is evident from Table 2, these modes mix with C–C stretching vibration 19*b* in PYR and PYR-d5, whereas in DFP the mode 9*b* mixes with C–C stretching vibration 19*b* and mode 18*a* mixes with C–F stretching vibration 20*a*.

The pair of bands near 245 and 346 cm^{-1} are assigned to C–F in-plane bending mode 9*a* and 18*b*, respectively, in DFP. The mode 9*a* mixes with C–C stretching mode 1, whereas the mode 18*b* mixes with mode 19*b*.

3.4. *C–H/C–D/C–F out-of-plane bending vibrations*

In PYR and DFP, the number of C–H out-of-plane bending modes, known as C–H waggings is 5 and 3, respectively, whereas in PYR-d5 the number of C–D out-of-plane bending modes is 5. They are designated as 5, 10*a*, 10*b*, 11 and 17*a* in PYR and PYR-d5, while in DFP they are identified as 5, 11 and 17*a*.

The bands at 942, 823 and 993 cm^{-1} are due to mode 5, whereas those at 749, 530 and 796 cm^{-1} are attributed to mode 11, while the absorptions near 891 and 690 cm^{-1} are assigned to mode 10*a*, whereas mode 10*b* is identified near 886 and 762 cm^{-1} in PYR, PYR-d5 and DFP respectively. It is interesting to note that all the five modes are pure in PYR and PYR-d5 except mode 11, which mixes with ring torsion 4. In DFP, the mode 11 mixes with C–F out-of-plane bending mode 10*b* and CCCC torsional mode 4, whereas the other two modes are pure.

The two C–F wagging modes are designated as 10*a* and 10*b* and identified near 501 and 227 cm^{-1} (calc. value) in DFP, respectively. The mode 10*a* is pure, whereas mode 10*b* mixes with ring torsion 16*b*.

3.5. *Ring torsions :*

The CCCC out-of-plane bending modes 4, 16*a* and 16*b* are known as ring torsions. The mode 4 is near 700, 567 and

720 cm^{-1} in PYR, PYR-d5 and DFP, respectively. Similarly, mode 16*a* is ascribed to the bands at 375, 327 and 219 cm^{-1}, whereas those due to mode 16*b* are identified around 405, 371 and 469 cm^{-1}, respectively in PYR, PYR-d5 and DFP. It is seen that the mode 4 is the highest ring torsion in the three molecules. It is pure in PYR, whereas in PYR-d5 and DFP it mixes with C–H/C–D out-of-plane bending mode 11. The present calculations establish that the frequency of mode 16*a* is less than that of 16*b* in the three molecules. The modes 16*a* and 16*b* have no mixing in PYR and PYR-d5, whereas it mixes with C–F out-of-plane bending mode 10*a* in DFP.

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